

**THE AQUEOUS SOLUBILITY OF TWENTY-SEVEN INSECTICIDES
AND RELATED COMPOUNDS.**

KEY WORDS: Impurities, multi-component solubility.

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ABSTRACT

The aqueous solubilities of 27 insecticides and related compounds were determined. Diazinon, fensulfothion and paraoxon had solubilities greater than reported in the literature. The presence of impurities and/or additional components in the mixture altered the measured solubility values. Addition of acetone in amounts up to 1% (volume) produced increases in parathion solubility up to 11%. The pH values of the equilibrated solubility systems were, in most instances, acidic and, in several instances, were in the pH 3-4 range.

INTRODUCTION

Aqueous solubility is one of the basic properties of pesticides which is useful in predicting their partitioning tendencies between the solid and liquid phases found in

the natural environment. Carringer et al (5) showed an inverse relationship between adsorption of several pesticides by organic matter and their aqueous solubilities. Chiou et al (6) derived an empirical equation relating experimental n-octanol/water partition coefficients (which have proved useful in predicting soil adsorption) to aqueous solubilities of a wide variety of chemicals, including organophosphorus pesticides.

A variety of methods has been used to obtain solubility data for organic pesticides. Basically, these methods can be grouped into two types: "analytical" and "synthetic". The former uses a saturated solution, prepared by using an excess of the compound. The undissolved compound and the saturated solution are separated and the saturation concentration measured. With the synthetic method, an excess of compound is weighed into solvent, and incremental additions of solvent are made until the concentration decreases. These methods have been extensively discussed (9, 10). The variations of these two basic approaches have produced some large discrepancies (10). Often workers have neither controlled the temperature at which measurements were made (i.e. room temperature) nor even reported it.

This study was undertaken to establish which solubility values reported in the literature could be duplicated in our laboratory. These data were needed to help predict the behavior of these compounds in soil systems under study.

MATERIALS AND METHODS

Compound Purity. The percent purity of the compounds is given in Table 1. Aminoparathion, obtained as the hydrochloride salt, and Fensulfothion were

TABLE 1. Aqueous Solubility of Insecticides and Related Compounds.

Compound	Physical State	Percent Purity	Temp. (°C)	Experimental		Solubility (µg/ml)
				Mean	Std.Deviation	Literature Citations
Bromophos	S	99	20.0	0.3	0.05	40 (7,11,18)
Carbofuran	S	99.2	19.0	320	34.	700 (18)
Chlorpyrifos	S	94	19.0	0.7	0.04	2 (18) ¹ , 0.47 (4)
Diazinon	L	99	22.0	68.8	2.8	40 (18) ³ , 40 (7)
Disulfoton	L	97.7	19.5	16.3	0.7	25 (7,18)
Disulfoton sulfoxide	L	90+	20.0	>4000		
Disulfoton sulfone	L	95+	20.0	883	61	
Ethion	L	95+	19.5	1.1	0.08	insol (7,18), 0.6 (15)
Fenitrothion	L		20.0	25.2	0.57	insol (18), 30 (7,14)
Fensulfothion	L	Purified (2)	20.0	2000	55.	1600 (7,18)
Fensulfothion sulfone	S	Recryst	20.0	74.6	1.0	
Fonofos	L	94.2	20.0	15.7	0.4	13 (18) ² , 13 (7) ¹
Fonofos oxon	L	94.4	20.0	>2600		
Iodofenphos	S	97.0	20.0	0.1	0.01	<2 (7,18)
Leptophos	S	100.	20.0	0.07	0.02	insol (18), .0047 (6), 0.03 (5), 2.4 (7)
Leptophos oxon	S	100	20.5	3.4	0.1	
Paraoxon	L		20.0	3640	109.3	2400 (19) ¹
Parathion	L	98.8	20.0	12.4	1.0	24 (7,14,18) 24 (19) ¹
Parathion, amino	L	Purified (3)	19.5	395.	7.7	
Parathion, methyl	S	Recryst	19.5	37.7	0.7	55 (7)
Phorate	L	99.9	20.0	17.9	2.2	50 (18)
Phorate sulfoxide	L		21.0	>8000		
Phorate sulfone	L		19.0	860	43.	
Ronne1	S	99+	20.0	0.6	0.07	40 (18), 1.08 (6), 44 (7)
Terbufos	L	Tech.	19.0	5.5	0.4	
Terbufos sulfoxide	L		20.0	>1100		
Terbufos sulfone	L		18.5	408	10.	

S = Solid, L = Liquid

¹ 25°C ² 22°C ³ Room Temp.

purified according to previous methods (2, 3 Fensulfothion sulfone and methyl parathion were recrystallized from methanol at -20°C. The percent purity of several compounds was unavailable so that they should be considered as being of technical purity.

Sample Preparation. The "analytical" method discussed earlier was used. Excess amounts of each compound were placed in 8 oz screw-cap (tin foil-lined) glass bottles. There were four replicates (except for four compounds in Table 1 whose solubilities exceeded the amount of available material, and therefore are indicated as "exceeding" a specified value). A common source of distilled water was used for the entire study. The volume of water used, per sample, varied from 100 to 300 ml, depending on the amount and solubility of available material. An effort was made to maintain at least a 3-fold excess of material. Preliminary studies showed excesses as great as 48-fold produced similar results to those samples having a 2-fold excess for bromophos, iodofenphos, and ronnel. The solutions were tumbled at 30 RPM and $20 \pm 1^\circ\text{C}$, and were sampled weekly until there were no further concentration changes. The samples were centrifuged in stainless steel tubes at either $34,800 \times g$ (Sorvall Model RC 2-B, SS-34 head) or at $159,315 \times g$ (Beckman Model L, Type II head) for 3 hours at $20 \pm 1.5^\circ\text{C}$. The temperature, measured following centrifugation, is the value shown in Table 1. At the final assay in each solubility experiment it was confirmed that an excess was still present in the sample.

An experiment was conducted to test the effect of acetone on the solubility of parathion in water. Parathion solubility was determined in duplicate at 0, 0.10, 0.25,

0.50 and 1.0% acetone(by volume). The samples were centrifuged at 18°C.

Analytical. Two automated gas-liquid chromatography (GLC) systems (autosampler, GLC, computing integrator, recorder) were used for analysis of the samples (triplicate Injections). One system was equipped with an alkali flame ionization detector (AFID) and the other system with an in-series electron capture detector (ECD) -AFID. Standards were interspaced among samples and also injected in triplicate. With the exception of paraoxon, leptophos, and leptophos oxon, the samples were injected as aqueous methanol mixtures (3, 17). The lower sensitivity of the above three compounds necessitated extracting them into chloroform, evaporating off the chloroform and dissolving them in a small volume of hexane for injection.

DISCUSSION

Solubility values for the 27 compounds (Table I) were obtained by centrifuging at 34,800 x g using the Sorvall Model RC 2-B high speed centrifuge. There was no apparent reduction in solubility of the compounds in the Beckman Model L ultracentrifuge at 159,315 x g. The temperature in both of these centrifuges was difficult to control within 1.5°C, and there appeared to be as much variation in solubility due to temperature fluctuations as there was to differences in centrifugal forces. Theoretically, particles larger than 150A⁰ and 408A⁰ should have been thrown down by the Beckman Model L, and the Sorvall Model RC2-B, respectively, in the three hour time period, assuming a specific gravity of 1.2 g/cc for the compound, T=20°C, RPM-17,000 (Sorvall) or 50,000 (Beckman). Since most of the

compounds were liquids, it is possible that undissolved droplets may have coalesced and been thrown down by either centrifuge.

Purity affected solubility in both instances. The solubility of carbofuran was 267 and 320 $\mu\text{g/ml}$ for 95.4 and 99.2% purity, respectively. However, with methyl parathion, the solubility decreased from 56 to 37.7 $\mu\text{g/ml}$ when the technical grade product, containing xylene as the major impurity, was recrystallized. Impurities may be a major contributing factor to the great discrepancies in reported solubility values in the literature. When possible, quoted solubility values should also include some mention of the compound purity.

There were numerous differences between solubility values obtained in this study and those quoted in the literature. Diazinon (68.8 $\mu\text{g/ml}$), paraoxon (3640 $\mu\text{g/ml}$) and fensulfothion (2000) $\mu\text{g/ml}$) were more soluble than reported in the literature (Table 1). The solubility of parathion was only half that quoted by Williams (19), but the paraoxon value was 50% larger. The parathion value was determined at 20°C, whereas Williams' value was at 25°C. Two similar compounds, ronnel and bromophos had reported solubilities of 40 $\mu\text{g/ml}$. However, our results indicated solubilities of 0.3 to 0.6 $\mu\text{g/ml}$, much more in line with a third related compound, iodofenphos, at 0.1 $\mu\text{g/ml}$. Carbofuran was about one-half as soluble as reported in the literature (18). It is interesting to note the general solubility relationship between related sulfides, sulfoxides, and sulfones, with solubility decreasing in the following sequence: sulfoxide > sulfone > sulfide.

Equilibrium pH values of the solubility samples tended to be acidic. It is not certain whether this acidity developed during the equilibrium period, or was due to impurities present in the original sample. A number of samples had pH values in the

3 to 1 range. Further studies are being conducted to determine if the pH decreases immediately on addition of the insecticide to the distilled water, which would suggest that impurities in the formulation were responsible for the pH decrease.

Researchers have sometimes added organic solvents, such as acetone, to increase the solubility of pesticides being used in aqueous adsorption studies (8, 12, 13, 16). The question arises as to whether the partitioning tendencies of the pesticide would be altered in the presence of the organic solvent. An experiment was conducted to determine whether acetone added in amounts up to 1% by volume would alter the solubility of parathion, which might affect its partitioning tendencies in a soil-water system. Parathion solubility increased with increasing acetone content, with an 11% increase in solubility being found for in 1% acetone addition. It would appear that for parathion, a considerable amount of acetone would be required to greatly increase its water solubility. Even at 1% acetone, the concentration ratio of acetone to parathion was approximately 800:1.

A multi-component solubility experiment was conducted to determine the effect of other components on solubility. Three compounds were selected: ronnel (0.6 $\mu\text{g/ml}$), chlorpyrifos (0.7 $\mu\text{g/ml}$) and bromophos (0.3 $\mu\text{g/ml}$). The solubilities of all three compounds increased when excesses of each were present i.e. ronnel - 1.36, chlorpyrifos - 1.0, bromophos - 0.5 $\mu\text{g/ml}$ (20°C). Although all three insecticides are solids, when introduced in combination (in excess), a liquid globule formed on the bottom of the glass bottle. In a second multi-component experiment, excess methyl parathion and fensulfothion sulfone were added in combination for a solubility determination. Reference samples of each compound were equilibrated simultaneously. The solubilities of methyl parathion and fensulfothion sulfone

(separately) were 45.8 and 81.8 $\mu\text{g/ml}$, respectively, as opposed to 37.7 and 68.4 $\mu\text{g/ml}$ when equilibrated together. The temperature recorded for this experiment was 21°C, thus accounting for the differences in values from Table 1. In this case, the solubilities of both components decreased. In a third multi-component solubility experiment, an excess of parathion and methyl parathion were equilibrated together. The solubilities of parathion and methyl parathion, respectively, were 5.2 and 39.3 $\mu\text{g/ml}$, compared with 11.1 and 44.5 $\mu\text{g/ml}$, respectively when determined separately. The temperature of this experiment was 20.5°C. The solubilities of both compounds decreased as was the case in the second experiment, but in this case the parathion solubility decrease was proportionally greater. These results suggest that the solubility of an organic compound may be altered in the presence of other compounds at their respective solubility levels. This reinforces the comments made earlier regarding the variable effect of impurities on the solubility of pesticides and their metabolites.

CONCLUSIONS

The aqueous solubilities of 27 insecticides and related compounds were determined. Diazinon, paraoxon and fensulfothion had solubilities considerably greater than reported literature values. Five compounds had smaller solubility values than reported in the literature. the presence of impurities and/or additional compounds in solution altered the solubility of a compound. Acetone (1% by volume) increased the solubility of parathion 1% in distilled water.

It is suggested that, when reporting solubility values, both temperature and sample purity be noted.

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